NUMERICAL PROBLEMS IN CALCULATING ELECTRONIC STRUCTURE OF ONE-DIMENSIONAL CHAINS

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I. INTRODUCTION

The purpose of this lecture is to provide simple applications on concepts presented in the introductory lectures\(^1,2\) on polymer calculations. It is also an attempt to point out some numerical problems occurring in one-dimensional periodic systems. The three following topics will be considered:

i. The Calculation of the Density Matrix Elements
ii. The Calculation of the First Derivative of the Energy Bands and the Band Indexing Problem.
iii. The Calculation of the Density of Electronic States

Before going through these subjects, it could be useful to define some quantities in the framework of the LCAO-(SCF)-CO formalism together with the notation used in this text, for more details see references 1 and 2.

The polymeric orbitals, \(\phi_n(k,r)\), are expressed as a periodic combination of atomic functions, \(\chi_p(r-j\alpha)\):

\[
\phi_n(k,r) = (2N+1)^{-1/2} \sum_{j=N}^{+N} \sum_{p=1}^{\omega} \exp(ikj\alpha) C_{np}(k) \chi_p(r-j\alpha) \tag{1}
\]

The coefficients, \(C_{np}(k)\), are obtained by solving the generalized eigenvalue problem:

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\[ F(k) \underline{c}_n(k) = S(k) \underline{c}_n(k) E_n(k) \quad (2) \]

where the column vector \( \underline{c}_n(k) \) contains the LCAO coefficients, \( \{ c_{np}(k) \} \), of \( \phi_n(k, \mathbf{r}) \).

The Fock and overlap matrix elements, \( F_{pq}(k) \) and \( S_{pq}(k) \) are expressed as follows:

\[ F_{pq}(k) = \sum_j \exp(ik_{ja}) F_{pq}(j) \quad (3a) \]

and

\[ S_{pq}(k) = \sum_j \exp(ik_{ja}) S_{pq}(j) \quad (3b) \]

\( F_{pq}(j) \) and \( S_{pq}(j) \) are respectively the Fock and overlap elements between atomic functions.

The density matrix elements, in the direct space, are defined as:

\[ D_{pq}(j) = a \frac{\pi/a}{2 \pi} \sum_{n=1}^{n_f} c_{np}^\ast(k)c_{nq}(k) \exp(ik_{ja}) dk \quad (4) \]

\( n_f = \) number of doubly occupied levels at a specific \( k \)-point.

The band structure can also be obtained using the expectation value equation:

\[ E_n(k) = \underline{c}_n^\ast(k) F(k) \underline{c}_n(k) \quad (5) \]

Finally, the density of electronic states, which is the number of states in the energy range \( E \) to \( E + dE \), for unit "volume" of the polymer, is written as:

\[ D(E) = \frac{1}{\pi} \sum_{n=1}^{n_f} \frac{dE_n(k)}{dE_n(k)} E_n(k) = E \quad (6) \]

II. THE DENSITY MATRIX

IIa. Definition and Usefulness

Density matrix in \( k \)-space is defined as:

\[ \underline{D}(k) = \underline{c}(k) \underline{c}^\ast(k) \quad (7) \]

where \( \underline{c}(k) \) is a \( \omega \times n_f \) matrix containing the \( n_f \) doubly occupied vec-